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MAGNESIUM OXIDE BY USING ELECTRON
PARAMAGNETIC RESONANCE

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ABSTRACT

A

This investigation is a study of the ultraviolet-irradiation-induced catalytic activity of MgO and the electron paramagnetic resonance spectra on the same sample. The data show that a correlation exists between the V_1 center concentration and the enhanced catalytic activity for the hydrogen-deuterium exchange reaction, $H_2 + D_2 \rightleftharpoons 2HD$. Samples were subjected to (a) degassing at 290° and 500° C, (b) thermal decay at -79° , 0° , and 30° C, (c) 2537 \AA UV as a function of time, and (d) several wavelengths of UV light. It is concluded that either a V_1 -type center existing on the surface is an active site for the exchange reaction, or the V_1 center formation is an integral step in the formation of the active site, that is, it is a hole trap that prevents recombination.

INTRODUCTION

Previous work¹ showed that the catalytic activity of MgO powders for the hydrogen-deuterium reaction $H_2 + D_2 \rightleftharpoons 2HD$ can be enhanced by ultraviolet irradiation provided that the catalyst is not completely degassed. The present investigation is a study of the induced catalytic

¹Lunsford, J. H., and Leland, T. W., J. Phys. Chem., 66, 2591, (1962).

activity and electron paramagnetic resonance (EPR) spectra on the same sample. Magnesium oxide catalysts are particularly suitable for such studies since the EPR spectra of MgO single crystals have been extensively explored by Wertz and coworkers.²⁻⁴

The role of unpaired electrons in adsorption on metals has been elucidated by the work of Selwood⁵ and others, who used magnetization techniques. Kohn⁶ observed the interaction between paramagnetic centers in silica gel and adsorbed gases, while Kokes⁷ made a similar study on zinc oxide. It follows that some such centers may act as catalytic sites. From a comparison of EPR data on irradiated single crystals it was suggested in an earlier paper¹ that the active site following irradiation was Fe⁺³. The present investigation has shown that the Fe⁺³ concentration actually decreases upon irradiation for the powders of catalytic interest. Subsequent data in this paper shows, however, that a correlation does exist between the V₁ center concentration and the irradiation-induced catalytic activity.

²Orton, J. W., Auzins, P., Griffiths, J. H. E., and Wertz, J. E., Proc. Phys. Soc. (London) 78, Pt. 4, 554 (1961).

³Wertz, J. E., Auzins, P., Griffiths, J. H. E., and Orton, J. W., Faraday Soc. Disc., 26, 66 (1958).

⁴Wertz, J. E., Orton, J. W., and Auzins, P., J. Applied Phys., Vol. 33, 322 (1962). (Supplement to vol. 33.)

⁵Selwood, P. W., Adsorption and Collective Paramagnetism, Academic Press, New York (1962).

⁶Kohn, H. W., J. Chem. Phys., 33, 1588 (1960).

⁷Kokes, R. J., J. Phys. Chem., 66, 99 (1962).

The V_1 center is defined in Fig. 1 as a hole trapped at an anion adjacent to a positive ion vacancy. Several conditions must be satisfied for the V_1 center to be formed, (a) charge compensation for the positive ion vacancy, (b) quanta of light with sufficient energy to free an electron, and (c) an electron trap. Irradiation removes electrons from the valence band, and the resulting electron hole (called simply a hole) is then free to move through the lattice until it is trapped at the positive ion vacancy. This center now has an unpaired electron that may be detected by EPR techniques.

EXPERIMENTAL

The catalysts used in this investigation were prepared from "reagent grade" MgO. Most of the experiments were carried out on pellets that were made from a paste of the powder and distilled water. The pellets, hereafter called P-1, were dried in air at 100° C and evacuated at $290^\circ \pm 5^\circ$ C or $500^\circ \pm 5^\circ$ C. Some data were obtained on the original powder, P-2, after evacuation at the elevated temperatures. A third sample, P-3, was doped by impregnation with 35 ppm Fe and fired at 800° C in vacuum.

Batch reactions were carried out in quartz and Vycor reactors with a volume of about 10 cc. The pressure of the reacting mixture was 20 mm Hg. All rate measurements reported here were carried out at -78° C and are expressed by a first-order rate constant. The gas samples were analyzed for percent HD with a mass spectrometer.

The ultraviolet lamps were of (a) a hot-cathode-type, mercury-argon discharge tube with the inner wall coated with a conversion

phosphor having its output in the range of 3100 to 4000 Å and (b) a hot-cathode-type tube with peak output at 2537 Å. The longer wavelength lamp was used in conjunction with a filter that removed the 3125 Å lines from the spectrum. All irradiations were carried out at $23^{\circ}\pm3^{\circ}$ C.

The EPR spectrometer used for this investigation was a Varian Model V-4500 equipped with a 100 kc modulation unit. The cavity resonance frequency was about 9500 Mc/sec. Measurements were made near 77° K by passing dry-nitrogen gas through a liquid-nitrogen heat exchanger and then past the sample.

THE EPR SPECTRUM

If the trapped hole in Fig. 1 is localized upon one oxygen ion for a time that is long compared with 10^{-7} sec, then the defect shows axial-electric-field symmetry with the principal axis of the crystal as symmetry axis.⁴ Wertz⁴ has observed the spectrum of the V_1 center, which can be described by $g_{\parallel} = 2.0032$ (magnetic field along the symmetry axis) and $g_{\perp} = 2.0385$ (magnetic field perpendicular to the symmetry axis). The lines broaden at temperatures higher than 77° K and cannot be observed after the irradiated sample has been heated to 100° C for a few minutes.

The shape of the paramagnetic resonance absorption curve for such a center in a polycrystalline sample is treated elsewhere.^{8,9} For $g_{\perp} > g_{\parallel}$ the derivative of the absorption curve will show a maximum at g_{\perp} and a minimum at g_{\parallel} .

The derivative spectrum of P-1 after UV irradiation at 2537 Å is

⁸Sands, R. H., Phys. Rev., 99, 1222 (1955).

⁹Kasai, P. H., Phys. Rev., 130, 989 (1963).

shown in Fig. 2. Arrows depict the g components reported by Wertz. A symmetric line is slightly to the low-field side of the g_{\parallel} minimum. In addition to the similarity of g -values to those observed by Wertz, the relaxation times for the irradiation-induced center are so short that the spectrum can be observed only near 77° K; hence, one may conclude that the V_1 center is being observed in the catalyst sample. The line at the higher field is due to Cr^{+3} , which is saturated with microwave power.

At present, it is not clear whether there is any contribution to the spectrum from V_1 -type centers existing on the surface. By definition the V_1 center cannot be a surface defect; however, a hole-trapping center at the surface, as shown in Fig. 1, may have an EPR spectrum which is quite similar to the V_1 center in the bulk. Experimental evidence is not conclusive. At about 20 mm Hg pressure and -78° C, H_2 , O_2 , or CO_2 have little or no effect on the spectrum shown in Fig. 2. On the iron-doped sample, P-3, H_2 and O_2 destroy the V_1 center spectrum in a few seconds. The V_1 centers are apparently formed in the iron-doped sample degassed at 800° C because Fe^{+3} ions act as charge-compensating centers for the magnesium ion vacancy.

RESPONSE OF V_1 CENTER CONCENTRATION AND CATALYTIC

ACTIVITY TO VARIOUS TREATMENTS

In an attempt to show that the enhanced catalytic activity is related to the V_1 center concentration, the samples were subjected to the following treatments: (a) degassing at 290° and 500° C, (b) thermal decay at -79° , 0° , and 30° C, (c) 2537 \AA UV as a function of time, and

(d) Several wavelengths of UV light. Unless otherwise indicated these treatments were carried out on P-1.

When the samples were degassed at 290° C and then irradiated with 2537 Å UV light, the catalytic activity increased about tenfold over the unirradiated samples, and the V_1 center spectrum appeared. The catalytic activity of the samples degassed at 500° C and irradiated showed no change in activity and no V_1 center spectrum. The effect of degassing at 290° C is to partly remove surface and interlattice hydroxyl groups. The remaining hydroxyl ions probably act as charge-compensating centers for the positive ion vacancies. Their role as electron acceptors during irradiation is also possible. When these hydroxyl groups are removed by degassing at higher temperatures, the cation vacancies are no longer stable.

The decay in catalytic activity and V_1 center concentration was followed at three temperatures following 2537 Å UV irradiation. The sample had been degassed at 290° C and in most cases the catalytic and EPR measurements were made successively. To prevent bleaching with room lights, the samples were kept in partial darkness. Results of these thermal decay experiments are shown in Fig. 3, where Δk_o and V_o are the enhanced rate constant and V_1 center concentration immediately after irradiation.

Response of the catalytic activity and V_1 center concentration to 2537 Å UV irradiation is shown in Fig. 4. In this case the sample was irradiated for 0.5, 4.5, and 45 min with the EPR spectrum recorded after each irradiation interval. The catalyst was then heated to 200° C to

remove any effects of the first UV treatment. Catalytic activity measurements were made after the same intervals of irradiation. While some scatter exists in the data, it is observed that more than half of the change takes place in the first 30 seconds of irradiation.

Various wavelengths of light were used for irradiation to determine qualitatively the threshold energy for the formation of the V_1 center and the enhanced activity. The intensity of the various portions of the spectra was not necessarily the same. The data show that

a wavelength of light less than 3200 Å is required to form the V_1 center and the active site. The cutoff wavelength seems to be about 3100 Å or 4 ev. This confirms earlier work¹⁰ which showed that a Pyrex reactor which acts as a filter of 50 percent efficiency for 3100 Å light reduces the enhanced catalytic activity considerably.

Catalyst P-2, which can be compared with that used in earlier work,¹ was subjected to similar tests, and qualitatively the agreement between catalytic activity and V_1 center concentration was substantiated. For this powder, however, a considerable error was introduced into the measurements since the V_1 center line was not more than five times the noise level. The preirradiation activation energy at -78° C for the exchange reaction was 5 and 0.6 kcal/g-mole for P-2 and P-1, respectively. One would not necessarily expect the same response to irradiation for different catalysts.

DISCUSSION OF RESULTS

Perhaps the strongest evidence that the active site for catalysis is closely related to the V_1 -type center comes from the thermal decay data. A decay scheme has been proposed for MgO single crystals by Soshea, Dekker, and Sturtz¹¹ that can be adapted to the present experiment. Irradiation with UV presumably produces a number of trapped electrons and holes resulting in a band scheme as shown in Fig. 5. At a given temperature the electrons trapped at E levels or holes at H levels (V_1 centers) will be released thermally.

¹⁰Lunsford, J. H., Ph.D. Thesis, Rice University (1961).

¹¹Soshea, R. W., Dekker, A. J., and Sturtz, J. P., J. Phys. Chem. Solids, 5, 23 (1958).

Let N be the total number of E levels and let $n(t)$ of them be occupied by electrons. The probability for an electron thermally released from an E level to combine with a trapped hole is p ; the probability for this electron to return to an E level is then $1 - p$ where

$$p = \frac{\alpha n}{\alpha n + \beta(N - n)} \quad (1)$$

Here, α is the cross section for trapping of an electron by a V_1 center, and β is the same quantity for an E level. Equation (1) implies that the cross sections α and β are large compared with those of other electron sinks. Experiments on the catalysts indicate that this is the case for temperatures less than $100^\circ C$. The rate of decay of electrons will therefore be equal to the rate of decay of V centers. This decay is determined by

$$\frac{dn}{dt} = -\gamma pn \quad (2)$$

where γ is a proportionality constant depending on temperature. The solution of the equation obtained by substituting (1) into (2) may be written as

$$t = C_1 \ln[n/n(0)] + (C_2/n)[1 - n/n(0)] \quad (3)$$

where $C_1 = (\beta - \alpha)/\gamma\alpha$ and $C_2 = \beta N/\gamma\alpha$.

The curves for decay at 0° and $30^\circ C$ shown in Fig. 3 are equation (3) fitted to the experimental data. It is important to note that while the loss of V_1 centers correlates quite well with the catalytic activity, there is a possibility that the E levels are the active sites. Wertz and co-workers¹² have shown that the formation and decay of Fe^{+1} ions in

¹²Wertz, J. E., Auzins, P., Griffiths, J. H. E., and Orton, J. W., Faraday Soc. Disc., 28, 136 (1959).

single crystals are similar to those of the V_1 center. They, along with others,^{11,13} have suggested that these ions might be the filled E levels. The author has also observed the Fe^{+1} ion spectrum in single crystals at 4° K following UV irradiation, but the spectrum has not been found in powder samples that show the V_1 spectrum.

The problem is then to decide whether a V_1 -type center is the irradiation-induced active site for catalysis or whether it is related only in an indirect manner. The fact that the V_1 center interacts quite strongly with H_2 in the P-3 sample indicates an affinity of the center for H_2 . It is recognized, of course, that the formation of very strong bonds between the reaction products and adsorbent is not conducive to high catalytic activity. Perhaps, because of structural differences, the bonds between P-1 and H_2 are weaker than the bonds between P-3 and H_2 and the equilibrium reaction



is shifted to the left so that the change in the number of V_1 -type centers is not detected upon exposure of P-1 to the reactants. This is tantamount to saying that $H \cdot V$ is a reaction intermediate of low concentration.

In a more general sense, this work confirms that the enhanced catalytic activity is directly related to an electronic phenomenon. This proposition has been set forth by several investigators for insulator

¹³Peria, W. T., Phys. Rev., 112, 423 (1958).

type catalysts.¹⁴⁻¹⁶ Furthermore, in light of the results reported here it seems most difficult to support an alternative mechanism which supposes that irradiation simply moves OH groups from active sites to inactive sites, and that at some later time these poisons diffuse back. It is possible that hydroxyl groups at the surface act as the primary electron traps and that these are the active sites. Such centers would be expected to show an EPR signal that could be correlated with the enhanced activity, but no such signal was observed in samples degassed at 290° C.

CONCLUSIONS

1. The experimental data show that a correlation exists between the UV irradiation enhanced catalytic activity and the V_1 center concentration.
2. This correlation strongly suggests that either a V_1 -type center existing on the surface is an active site for the hydrogen deuterium exchange reaction, or the V_1 center formation is an integral step in the formation of the active site, that is, it is a hole trap which prevents recombination.

¹⁴Kohn, H. W., and Taylor, E. H., J. Phys. Chem., 63, 500 (1959).

¹⁵Kohn, H. W., and Taylor, E. H., Paper No. 71, Proc. Intern. Cong. on Catalysis, 2nd., Paris, 1960, 2, pp. 1461-1480.

¹⁶Kazanskii, V. B., and Pecherskaya, Yu I., Russian J. of Phys. Chem., 34, 225 (1960).

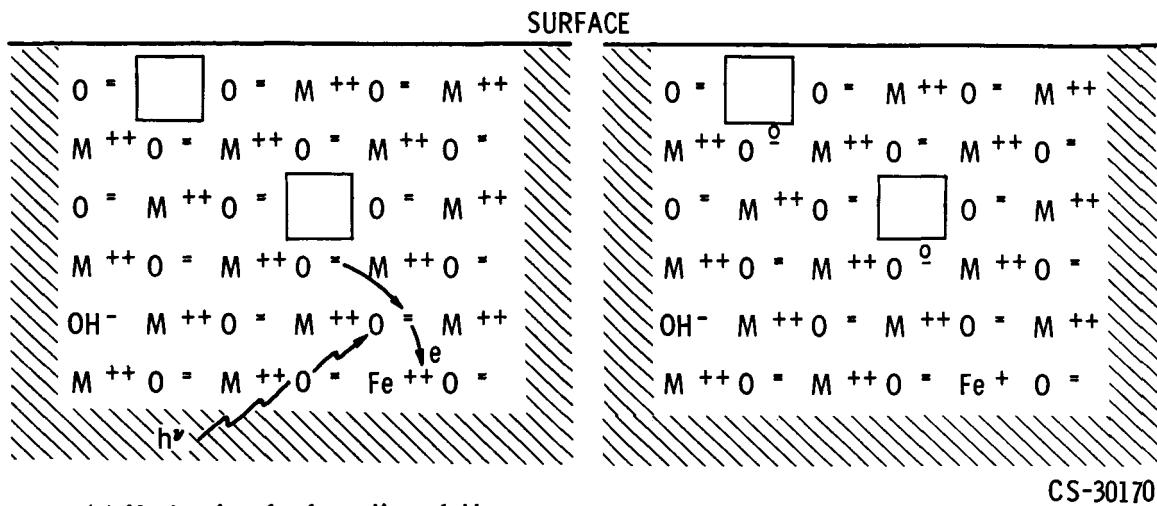
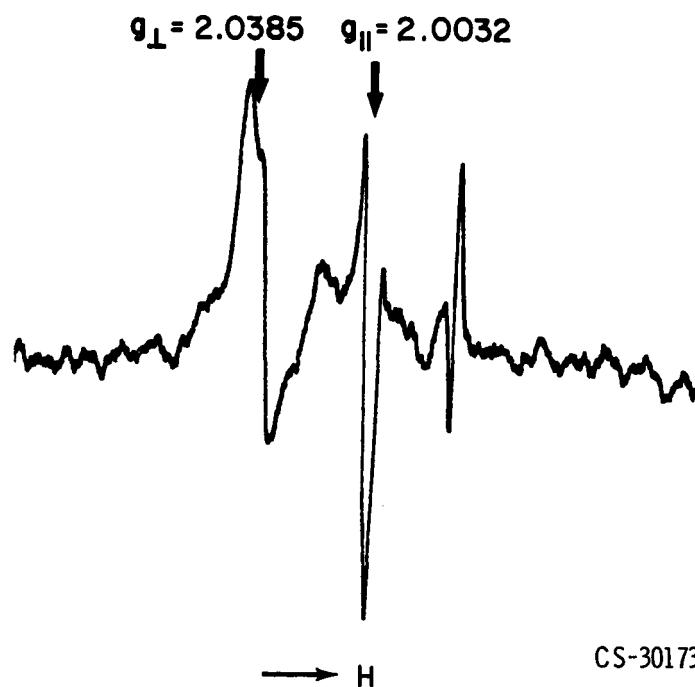


Figure 1. - Metal-oxide lattice showing V_1 center, electron trap, and charge compensating ion.

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Figure 2. - Spin resonance curve of MgO catalyst de-gassed at $290^{\circ}C$ in vacuum and irradiated with 2537 \AA ultraviolet light.

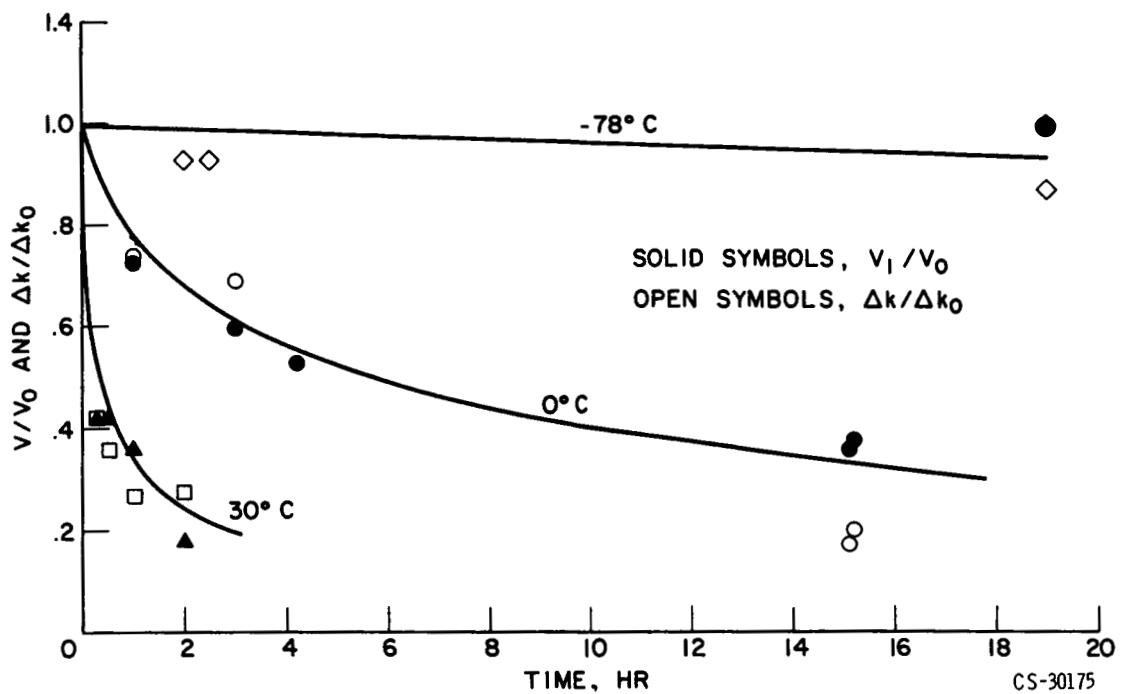


Figure 3. - Thermal decay at three temperatures following 2537 \AA ultraviolet irradiation. The curves at 0° and $30^\circ C$ represent equation (3) with the constants C_1 and C_2 fitted to the experimental points.

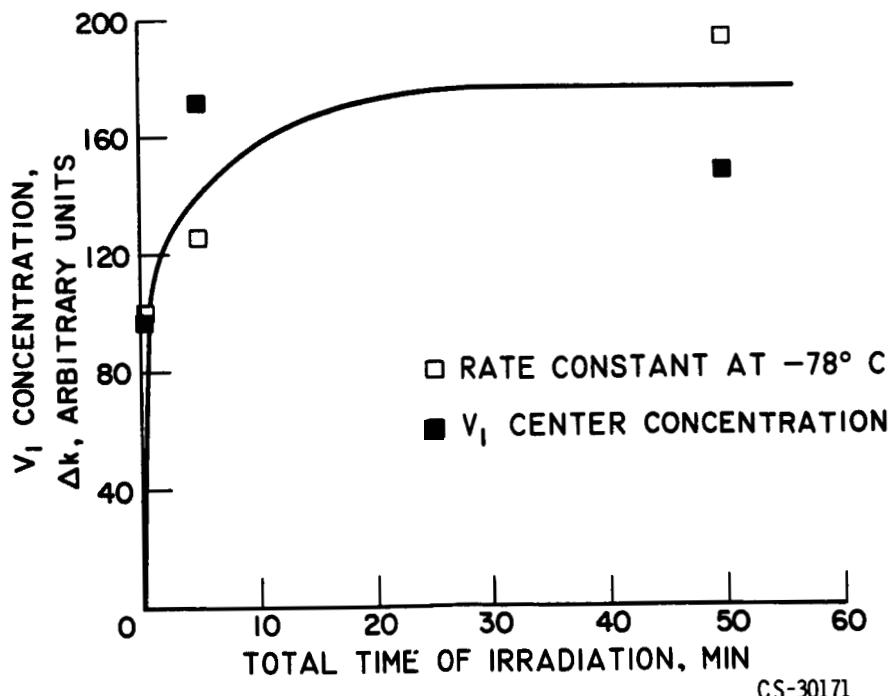


Figure 4. - Response of catalytic activity and V_1 center concentration to 2537 \AA irradiation at $23^\circ C$.

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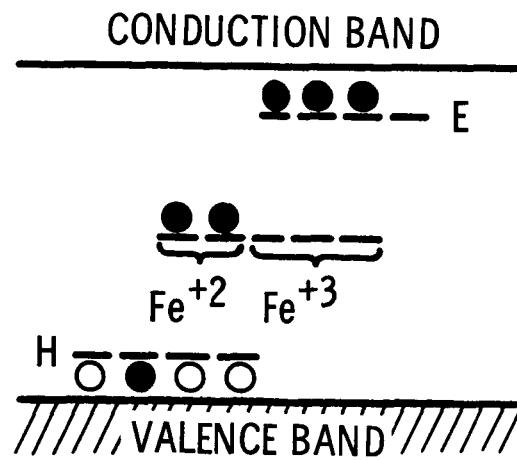


Figure 5. - Schematic energy-level diagrams for irradiated MgO. The levels E and H are, respectively, electron and hole traps. (After Soshea, Dekker and Sturtz, ref. 11.)